

A STUDY OF BAKING OVEN VAPORS

by

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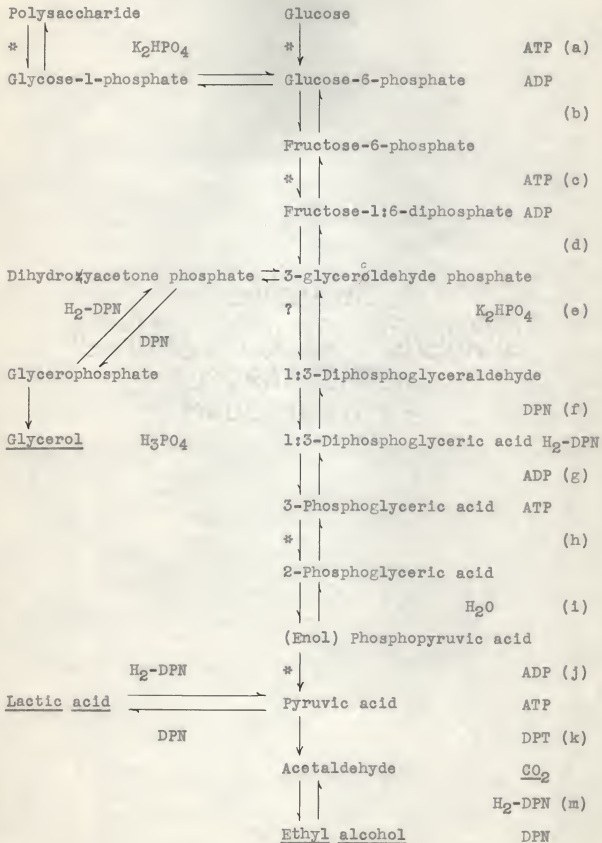


## INTRODUCTION

The constituents of bread flavor are at present unknown factors and therefore the study of bread baking vapors was thus undertaken to chemically characterize the constituents of bread flavor. The study of all vapors given off during the baking of bread should also give much useful information and should be an aid to the study of the mechanism of the general dough fermentation process.

A search of the literature reveals no previous work on the subject of oven vapors. To gain preliminary information as to what possible gases might be present in the baking oven vapors, the author has referred to the process and mechanisms of alcoholic fermentation. Embden-Meyerhof-Parnas have presented the following scheme for the alcoholic fermentation process (Porter, 9).

## Scheme of Embden-Meyerhof-Parnas



*	= Mg++ or Mn++ ions required
ATP	= adenosine triphosphate
ADP	= adenosine diphosphate
$K_2HPO_4$	= inorganic phosphate
?	= reaction not definitely proved
DPN	= diphosphopyridine nucleotide
$H_2$ -DPN	= reduced diphosphopyridine nucleotide
DPT	= diphosphothiamin

Although the foregoing reactions account for the main products in alcoholic fermentation, ethyl alcohol and carbon dioxide, they do not account for them all. Carbon dioxide is given off from the system in reaction k, forcing the over-all reaction to completion in this direction. The degree of completion of reaction k is not 100 percent, and reaction m will approach equilibrium conditions, and hence, pyruvic acid, acetaldehyde, and ethyl alcohol are always present and are subject to other reactions.

Formic, acetic, and succinic acids, 2-3 butylene glycol, fusel oils, and other compounds have been shown to occur as by-products of alcoholic fermentation (Tables 1 and 2). Reactions have been suggested to account for these products, but in some cases they have not been proved experimentally. For example, acetic acid may arise from the dismutation of acetaldehyde as suggested by Neuberg (Porter, 9) or it may be formed from pyruvic acid by the following reaction, which would also account for formic acid (4).

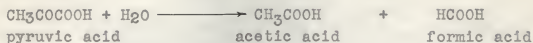
Table 1. Byproducts of alcoholic fermentation (from Joslyn, by Porter, 9).

Product	Theory	Industrial : ferment	Pasteur : data	Champagne : yeast	Rhotsitch : yeast	Steinberg : yeast
Alcohol	51.1	48.4	48.6	47.8	48.1	48.0
CO <sub>2</sub>	48.9	46.5	47.0	47.0	47.6	47.6
Acetaldehyde		0.8		0.01	0.04	0.02
Acetic acid		0.25		0.61	0.5	0.65
2,3 butylene glycol				0.06	0.09	0.10
Glycerol		3.6	3.1	2.99	2.61	2.75
Lactic acid		0.2		0.40	0.28	0.40
Succinic acid		0.6	0.6	0.03		0.04
Fusel oil		0.5				
Furfural		trace				

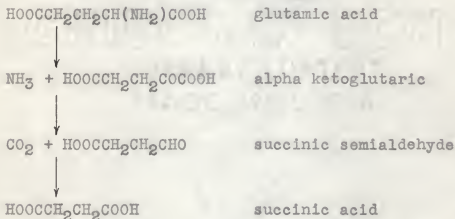
Table 2. Composition of fusel oil from various sources (from Jacobs and Newton, by Porter, 9).

Source :	Alcohol, percent				
	: n Propyl :	n Butyl :	Isobutyl :	n Amyl :	Isoamyl : Residue
Potatoes	3.9- 6.9		16.5-24.4	68.8-79.5	0.04-0.14*
Molasses	13.0		42.0	36.0	9.0
Brandy	11.7-12.1	0.0-63.8	0.0- 4.5	24.5-85.0	
Whiskey	1.7-20.4		12.2-23.9	14.6-23.4	36.3-59.7
Sugar	3.7	0.0	2.7	93.6	0.0

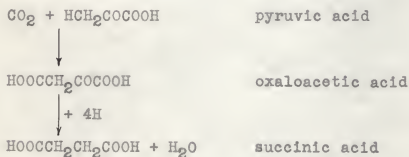
\* Hexyl alcohol demonstrated in one sample, and acids, esters and furfural in another.



Succinic acid has been thought to arise from glutamic acid during fermentation through the following series of changes (9):

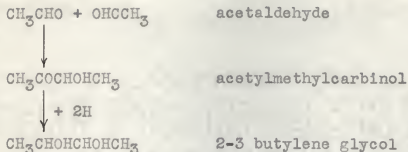


However, more recent studies by Wood and Werkman, according to Porter (9), show that succinic acid may also arise from pyruvic acid by the so-called carbon dioxide fixation reaction:

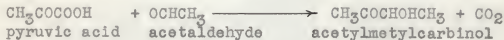


It has been suggested by Kluyver (7) and others that 2-3 butylene glycol may arise in fermentation by the condensation of two molecules of acetaldehyde, which is then reduced to 2-3 butylene glycol:

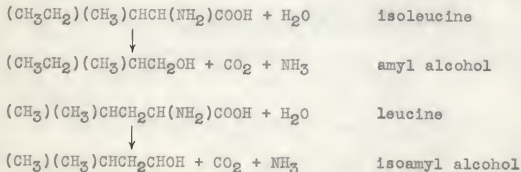




It is also probable that acetylmethylcarbinol, the precursor of 2-3 butylene glycol, arises from a condensation of pyruvic acid and acetaldehyde, as suggested by Green et al. (2). The reaction may be written as follows:



The composition of fusel oil formed in alcoholic fermentation has already been mentioned (Table 2). Although little experimental evidence is available concerning the source of the compounds which make up fusel oil, it is believed that certain of them arise from nitrogen metabolism, on the part of yeast. Amyl and isoamyl alcohol, for example, may be derived from the hydrolytic decarboxylation and deamination of the amino acids isoleucine and leucine, respectively:



In addition to those products produced by alcoholic fermentation process, baking itself may introduce other components (products) and/or interactions among the products of fermentation.

Reviewing these reactions and the products of these reactions the following table of products and their boiling temperatures which might appear in the baking oven vapors was prepared.

This list was not considered to be complete but merely to serve as a guide. It is also seen that from the products listed 32 esters are possible from the different combinations of 8 alcohols and 4 acids listed.

Considerations involved in collection of vapor samples for analysis and the analysis itself are complicated by the nature of the components of the baking oven vapors. The small concentration of the by-products of dough fermentation is even further diluted in the baking of bread because of the water driven off from the dough during baking.

In considering ways and means of collecting a sample from the baking oven gases, the chemical and physical nature of these gases must be considered along with the amount of gases to be collected. Chemically the gases are derived from the alcoholic fermentation process, from proteolytic action, and combinations of these products. All the baking oven vapors are volatile, naturally, at a temperature of 425° F.

Table 3. Products and their boiling point which might appear in the baking oven vapors.

Product	:	Boiling point °C. *
carbon dioxide		-78.5
formaldehyde		-21.0
acetaldehyde		20.2
methyl alcohol		64.7
ethyl alcohol		78.5
n-propyl alcohol		97.0
formic acid		100.0
iso butyl alcohol		107.3
iso amyl alcohol		113.0
n-butyl alcohol		117.7
acetic acid		118.1
lactic acid		122.0 (14 mm)
n-amyl alcohol		137.8
acetylmethylcarbinol		148.0
hexyl alcohol		157.2
furfural		162.0
pyruvic acid		165.0 (sl. d)
2-3 butylene glycol		178.6

\* Boiling points taken from Lang's Handbook, 6th ed.

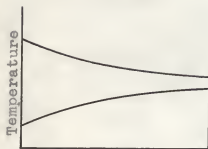
Rough approximations can be made as to the size of sample which should be collected, and the means best suited for its collection.

For one pound of baked bread, 510 gms of dough must be used. This amount of dough contains 12.2 gms of added sugar and approximately 6.1 gms (2 percent) of sugars occur in the flour, making a total of 18.3 gms of sugar available for fermentation. If the fermentation reaction approaches that of industrial fermentation, about 48 percent of the sugar fermented will be converted to ethyl alcohol, 47 percent to carbon dioxide, and 5 percent will be used to form by-products of the fermentation reaction. No information is available as to what fraction of the sugar available for fermentation is actually used, but a conservative estimate would be 50 percent. Therefore for each loaf of bread there would be produced 4.39 gms of ethyl alcohol, 4.30 gms of carbon dioxide and 0.46 gm of by-products. During the fermentation process considerable amounts of the more volatile products of fermentation are lost to the atmosphere. Again no exact information is available as to the percentage of such products lost but an estimate of 50 to 75 percent would not be unreasonable. This would result in a loss of 2.2 to 3.3 gms of ethyl alcohol plus some of the by-products. The maximum concentration of ethyl alcohol and by-products to be expected in the baking oven vapors would be 2-4 percent and 1 percent, respectively. From these approximations it was concluded that the vapor from 100 or more

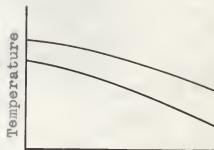
loaves of bread would have to be collected to obtain a workable sample which could be used for separation and analysis of the components of the baking oven vapors.

Collection of a gas sample may be achieved by: (1) Condensation, (2) Liquid absorption, (3) Solid adsorption, (4) Chemical reaction of the gases, and (5) A combination of the above.

Two types of collection of gas samples by condensation may be employed. These are parallel flow, in which the hot fluid and the cold fluid enter at the same end of the apparatus and flow parallel to each other through it, and counter-current or counterflow condensation in which the hot fluid enters one end of the apparatus and the cold fluid enters at the other, allowing the fluids to pass by each other in opposite directions. These arrangements of condensation may be represented by the following diagrams (1).

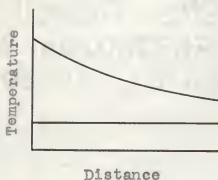


Distance  
Parallel flow



Distance  
Counter-current flow

In the case of countercurrent operation, the temperature drop along the length of the apparatus is more nearly constant than in the case of parallel flow. In countercurrent operation the exit temperature of the hot fluid can be considerably less than the exit temperature of the cold fluid, and accordingly a larger proportion of the heat content of the hot fluid can be extracted for a given entrance temperature of the cold fluid. To achieve cooler condensation temperatures, systems involving salt-ice brines or solid carbon dioxide in carbon tetrachloride may be used. In these systems the cooling temperature remains constant while the temperature of the hot fluid will approach that of the cooling system. Condensation systems of this type may be represented by the following type diagram (1).



It is noted that again there is an uneven temperature drop across the system. These types of condensation systems are special cases of the parallel flow condensation (even

though the cooling medium is at rest) and calculations for the systems are the same.

Gas absorption in the usual sense involves the transfer of gas from the gas phase into a liquid, in which it is more or less soluble. Three general cases may be distinguished as regards the nature of the gas and liquid involved (3).

1. A chemical reaction takes place, such that the gas will not exert an appreciable vapor pressure after absorption.

2. A chemical reaction takes place, but the compound formed is sufficiently unstable so that the dissolved gas exerts an appreciable vapor pressure.

3. No chemical reaction takes place, and the pressure exerted by the dissolved gas is dependent only on the concentration of the dissolved gas in the liquid.

Liquid absorption, as indicated in case 3, is limited to the equilibrium absorption of the gas in the liquid at that particular temperature and pressure. To enable equilibrium to be reached several types of absorption towers have been designed. One type of absorption tower is packed with inert, irregular shaped objects to allow more intimate contact of the gas and liquid. Absorption bubble cap towers have been designed similar to distillation towers. The absorption process may be either continuous or batch operation. In the problem presented here batch operation absorption would produce a more concentrated sample.



All gases or vapors tend to be adsorbed or condensed on the surface of any solid with which they are in contact. The phenomenon was first mentioned by Scheele, who reported the results of experiments on gases exposed to charcoal. It was shown by de Saussure that all kinds of gases are adsorbed by a variety of porous substances such as meerschaum, asbestos, wood, and charcoal (14).

Many industrial processes, from which objectionable odors or vapors are given off, use activated charcoal adsorption towers to eliminate these odors or vapors from their exhaust gases. In the process the carbon is revived after saturation has occurred by passing steam through the carbon adsorber and the distillate is condensed and either sent to the sewer or to some reclaiming process if the distillate is of any value (14). A similar process is used by the brewing industry to capture entrained alcohol from the fermentors (8).

There are six standard means of separation of organic mixtures:

1. Fractional distillation
  - a. direct distillation
  - b. steam distillation
  - c. distillation under reduced pressure
2. Extraction with solvents without chemical change
3. Extraction with solvents that produce chemical change
4. Fractional crystallization



#### 5. Chromatographic technics

#### 6. Combination of the above

The separation of organic acids by chromatography on paper has been described by Stock, Goodban, and Owens (13). In their method, the substances to be separated are applied to the paper as the free acids. Kennedy and Barker (6) have developed a technic for the separation and identification of volatile fatty acids in micromole quantities. In this method the volatile fatty acids are applied to the paper as the ammonium salts of the acids, and chromatograms are developed in solvents containing free ammonia, so that the acids are present at all times as the completely ionized ammonium salts.

### MATERIALS AND METHODS

#### Materials

Baking oven vapors were collected from bread produced with a moderately strong bread flour in the pilot plant bakery of Kansas State College Milling Industry Department.

All chemical reagents used in these experiments were of C. P. grades.

For the adsorption experiments C. P. grade activated charcoal, Duolite A-2, and Duolite C-3 anion and cation exchange resins respectively were used.

Whatman No. 1 filter paper was used in all paper chromatographic experiments.

The following commercial baking formula was employed:

Ingredient	Percent	Weight	
		Pounds	Ounces
Flour	100.00	18	0.00
Water	63.00	11	5.00
Milk	4.00		12.00
Shortning	4.00		12.00
Sugar	4.00		12.00
Salt	2.00		6.00
Yeast	2.00		6.00
Panipulus	0.50		1.50
Malt	0.25		0.75
Arkady	0.25		0.75

#### Methods

In these experiments baking oven vapors collected by three methods were studied. Preliminary experiments were designed to incorporate all three methods in one collection system. Two adsorption towers were prepared, one containing activated charcoal for solid adsorption, and the other ground porcelain for liquid absorption experiments. A series of large laboratory water cooled condensers were used for condensation of the vapors. A negative pressure system was used to draw the baking vapor through the collection apparatus. The baking oven vapors were first passed through the solid adsorption tower, then through the liquid absorption tower, and finally through the condensers.

The final experiments on collection were conducted on the condensation method alone. In addition to the water cooled condensers, the vapors were drawn through a salt-ice brine cooling bath and a Dewar flask containing dry ice in carbon tetrachloride.

The following organic class tests were used to prove the presence of specific classes of organic compounds in the various separation fractions (11).

Esters. To one drop of ester in a test tube, 0.5 ml of 1 N solution of hydroxylamine hydrochloride in methanol was added. Then enough 2 N potassium hydroxide in methanol was added to the solution to make it alkaline to litmus paper. The solution was heated just to boiling and then cooled. The solution was acidified with 5 percent hydrochloric acid and one drop of 10 percent ferric chloride added. A reddish-wine color is a positive test for esters.

Acids. To 100 mg (2 drops) of the acid, in a test tube, 5 drops of thionyl chloride are added. The test tube was immersed in boiling water for 15 to 30 seconds. Then 3 drops of alcohol (butyl or amyl) are added and the tube again immersed in boiling water for 30 seconds. The solution was cooled and 1 ml of water added to hydrolyze the excess thionyl chloride. This procedure converts the acid to its ester (butyl or amyl) and the ferric hydroxamate test for esters was performed.

Aldehydes and Ketones. Fifty mg of 2-4 dinitrophenylhydrazine were suspended in 10 ml of ethanol and the solution heated to boiling. Three drops of the aldehyde or ketone were added and the solution boiled for one minute. Then 3 drops of concentrated HCl were added and the solution boiled for 30 seconds. If no precipitate formed on cooling, water was added dropwise. A white or yellow precipitate is a positive test for aldehydes or ketones.

Schiffs Test. Three drops of the aldehyde to be tested were added to one ml of colorless Schiffs reagent. A wine-purple coloration developed within 10 minutes if the material being tested was an aldehyde.

Tollens' Reagent. In thoroughly clean test tubes 2 ml of 5 percent solution of silver nitrate was placed and one drop of 10 percent sodium hydroxide added. A very dilute solution of ammonia (2 percent) was added drop by drop, with constant shaking, until the precipitate of silver oxide just dissolved. In order to obtain a sensitive reagent it was necessary to avoid a large excess of ammonia. The 50 mg of the compound to be tested was added. If no reaction takes place the solution was warmed slightly. A black or silver precipitate was a positive test. The test is for easily oxidized compounds.

Alcohols. The xanthate test for alcohols was conducted by placing one pellet of solid potassium hydroxide in a dry test tube which contained 0.5 ml of the alcohol to be tested.

The mixture was heated until the potassium hydroxide dissolved. (Very volatile alcohols require a reflux condenser.) The solution was cooled and one ml of ether added. Carbon disulfide was added drop by drop until a pale-yellow precipitate formed. If a precipitate did not form by the time 0.5 ml of carbon disulfide had been added, the compound being tested was not an alcohol.

A confirmatory test for the xanthate produced was made by reacting it with a very dilute solution of molybdenum salts. The precipitated xanthate was separated from the test solution and about 5 mg added to 2 drops of a solution containing about one mg of ammonium molybdate. On the addition of 4 drops of 2 N  $\text{NH}_4\text{Cl}$ , a red-blue coloration develops if a xanthate is present.

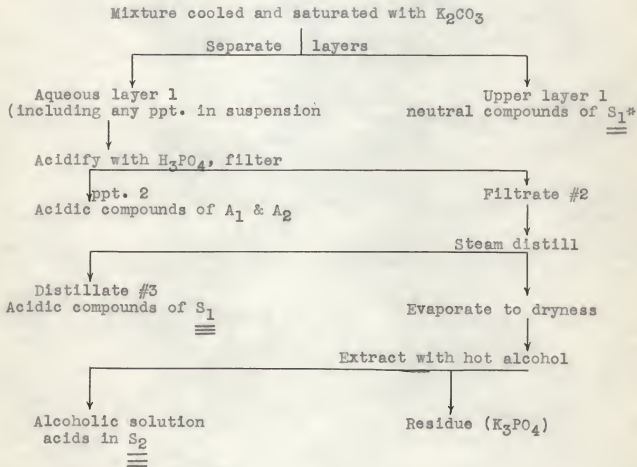
Test to Distinguish Primary, Secondary, and Tertiary Alcohols. (Applicable only to alcohols with less than six carbons.) A 0.5 ml aliquot of the alcohol was placed in a test tube with 3 ml of Lucas reagent. The tube was stoppered and shaken vigorously. The tube was allowed to stand at 25-30 °C. A reaction is detected by a clouding of the solution, due to the formation of an insoluble alkyl halide. Tertiary alcohols react immediately; secondary alcohols react within 2-3 minutes; primary alcohols require a much longer time.

The cloudiness of the solution will clear up on standing, and a separate layer of the alkyl chloride will form. If the separate layer does not form, it is likely that the alcohol

detected was only an impurity in a less reactive alcohol.

Distillation Procedures. The distillation procedures followed in these experiments were the normal distillation procedures encountered in the chemical laboratory. Experiments were conducted using direct (oil bath), vacuum, and steam distillation procedures.

The following schematic method of separation by Shriner and Fuson (11) for water-soluble mixtures containing esters was used.



\* See Table 3.

Table 4. Classification of organic compounds by solubility (Shriner and Fuson, 11).

Solubility class	Solubility	Types of compound	Volatility: alone	Volatility: with steam
S <sub>1</sub>	soluble in H <sub>2</sub> O and ether	low molecular weight alcohols, aldehydes, ketones, acids, esters, amines, nitriles, acid chlorides	readily dis- tilled	volatile with steam
S <sub>2</sub>	soluble in H <sub>2</sub> O but insoluble in ether	polyhydroxy alcohols, carbohy- drates, amine salts, metal salts, poly basic acids, hydroxy- aldehydes, hydroxy-ketones, hydroxy-acids, amino acids	low vola- tility excep- tions	not volatile with steam



Adsorption Procedures. Both batch and countercurrent adsorption procedures were employed in these experiments, using activated charcoal, duolite A-2, and duolite C-3 as the adsorbents. Duolite A-2 and duolite C-3 are anion and cation exchange resins, respectively, which were used to concentrate and separate the organic acid material from the other baking oven vapors.

Extraction with Solvents that Produce Chemical Change. The selection of derivatives for the separation and identification of organic mixtures is dependent upon the type of material involved and the form in which it is present (11).

Ester Derivatives. The most general method for identifying an ester consists in hydrolyzing it to the acid and hydroxy compound. Esters may be converted to amids by reaction with ammonia, or to N-benzylamids with benzylamine.

Acid Derivatives. Solid esters furnish a useful means for characterizing acids. Some methyl esters are solid but in most cases the p-nitrobenzyl, phenacyl, p-chlorophenacyl, p-bromophenacyl, or p-phenylphenacyl esters must be prepared to obtain solid esters. These are prepared by treating the salts of the acids with the corresponding halide.

Alcohol Derivatives. The most general derivatives of primary and secondary alcohols are the alpha-naphthyl-, p-nitrophenyl-, and phenylurethans. These are formed when the alcohol is treated with alpha-naphthyl, p-nitrophenyl, and phenyl isocyanates, respectively. Urethans are also



produced by treating alcohols with acid azides. The presence of water as an impurity in the alcohol causes some difficulty in obtaining urethans by either of these two methods. For water soluble alcohols likely to contain traces of moisture, the 3-5 dinitrobenzoates are generally more satisfactory than the urethans. The 3-5 dinitrobenzoates are made by treating the alcohols with 3-5 dinitrobenzoyl chloride.

Aldehyde and Ketone Derivatives. The most useful derivatives of aldehydes are the phenyl, p-bromophenyl, p-nitrophenyl and 2-4 dinitrophenylhydrazines. If, in the classification test with phenylhydrazine, a solid phenyl hydrazone is obtained, this will be used as a derivative. However, if the phenylhydrazone is a liquid, recourse must be had to one of the substituted phenylhydrazones; of these the 2-4 dinitrophenyl hydrazones are to be recommended because they are all solids.

For low-molecular-weight, water-soluble aldehydes, it is often advantageous to employ semicarbazide as the reagent. All the semicarbazones are solids and can generally be obtained more pure without recrystallization.

Sometimes these derivatives form slowly, and care must be taken to allow sufficient time for the reaction to go to completion. These carbonyl reagents may also be used to obtain solid derivatives of ketones (11).

Magnesium and Lead Acetate Precipitation of the Organic Acids. A common method of separating a mixture of acids is

the fractional precipitation method (10). This was carried out by treating the saturated alcoholic solution of the acids with several portions of alcoholic solutions of magnesium or lead acetate. The precipitate that first forms contains the acids of high molecular weight; each succeeding precipitate contains acids of smaller molecular weight. The precipitated salts of one fraction were filtered off before the next fraction was precipitated. On treatment with hydrochloric acid the salts liberated the free organic acid. The process was then repeated on the individual fractions until no further purification resulted.

Preparation of the Sodium Salts of the Acids. The sodium salts of organic acids were prepared by the careful neutralization of the acids with sodium hydroxide. The solution is then evaporated to dryness.

Chromatographic Technics. All chromatographic experiments were conducted in a large enclosed balance case, at room temperatures. The developing solvent was distributed throughout the case to cause saturation of the air by their vapor. Both ascending and descending uni-dimensional chromatograms were made. The ascending chromatograms, in addition to being placed in the case, were enclosed in two liter hydrometer jars, the developing solvent placed in the bottom and the top sealed. The length of time of development of the chromatograms was varied for each solvent used along with varying concentrations of the unknowns. The chromatograms were dried at room temperature

overnight or in an electric oven at  $80^{\circ}$  C. for five minutes.

Experiments were conducted on the filter paper as is, the paper prewashed with distilled water, and paper pretreated with one percent oxalic acid solution and then washed with distilled water. All paper that was washed before using was dried at room temperature overnight.

The known and unknown acid solutions to be separated were spotted on the paper by use of a 0.01 ml pipet. To obtain higher and varying concentrations of the unknowns, additional aliquots were placed one on top of another, allowing each application to dry before the next one was applied. The spots were placed on the paper two inches from the bottom for ascending columns and one-half inch down from the top on the descending chromatograms.

The unknown acid solutions were prepared for chromatographic separation by the following procedures, with chromatograms being developed for each method using all the different chromatographic techniques described: (a) The original condensate, (b) Concentration (10 times) and separation of the acid fraction of the condensate by use of an anion-cation exchange resins. (The anions are adsorbed on the anion exchanger, Duolite-A-2, and then eluted with either two percent sodium or ammonium hydroxide. The sodium or ammonium ions are then removed by adsorption on the cation exchanger, Duolite C-3.) (c) Neutralization of the acid fraction with sodium hydroxide and evaporating to dryness. The sodium salts of the acids

were then placed in water solution and equimolar amounts of ammonium sulfate were added plus a small amount of free ammonia. The sodium salt solutions were made of the concentration so that each 0.01 ml aliquot contained one micromole of acid.

The position of the acids on the chromatograms after development and drying were shown by spraying the paper with the appropriate indicator for the system of chromatography being employed. For those chromatographic systems using acid developing solvents, the paper was sprayed with bromocresol green, 400 mg per liter in 95 percent ethyl alcohol made slightly alkaline with sodium hydroxide. With this indicator the acid spots appeared yellow on a blue background (13). Those chromatographic systems employing basic developing solvents were sprayed with a solution of 50 mg of bromophenol blue in 100 ml of water, made acid with 200 mg of citric acid (6). Because of the buffer capacity of the acid anions, the location of the spots was shown by the intense blue (alkaline) color of the indicator, while the background was orange-yellow. Those chromatographic systems in which the ammonium salt of the acid is developed were optionally sprayed with a one percent ninhydrin solution and heated for five minutes at 80° C. The location of the acids was shown by purple or brown spots on a white background (5).

The following developing solvents were used:

1. Ethyl alcohol (95%); ammonium hydroxide, 1%.
2. n-Butyl alcohol, 95 ml; water, 5 ml; ammonium hydroxide, 1%.
3. n-Propyl alcohol, 10 ml; water, 1 ml; ammonium hydroxide, 1%.
4. Isopropyl alcohol, 1 ml; tertiary butyl alcohol, 1 ml; benzyl alcohol, 3 ml; water, 1 ml; ammonium hydroxide, 1%.
5. n-Butyl alcohol, 5 ml; benzyl alcohol, 5 ml; water, 1 ml; ammonium hydroxide, 1%.
6. n-Butyl alcohol, 4 ml; glacial acetic acid, 1 ml; water, 1 ml. (This solution must be freshly prepared for each determination.)
7. Tertiary butyl alcohol, 5 ml; benzyl alcohol, 15 ml; water, 2 ml; 90% formic acid, 1%.
8. Isopropyl alcohol, 1 ml; tertiary butyl alcohol, 1 ml; benzyl alcohol, 3 ml; water, 1 ml; 90% formic acid, 1%.
9. Phenol, 3 gms; water, 1 ml; 90% formic acid, 1%.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Collection of Baking Oven Vapors

Preliminary experiments were conducted on the collection of baking vapors using all three methods of collection; namely, liquid absorption, solid adsorption, and condensation. From these experiments water and other liquid absorbents were quickly eliminated as desirable means of vapor collection because liquid absorption could cause only further dilution of the baking oven vapors. Activated charcoal was eliminated as a

desirable means of collection for the same reason because the adsorbed material must be eluted by steam, thus diluting the minor oven vapors. Collection by chemical reaction of the baking oven vapors was deemed undesirable for future analysis, so the condensation method was reverted to.

Preliminary experiments were conducted on the regular gas fired oven of the pilot plant bakery. Since the condensation method of collection of vapors was thought the best to be employed, an experimental check was made to determine which type and in what quantity condensable flue gases were produced by the oven itself. It was found that 2.5 ml of water per minute was condensed from the gas combustion in the oven. Under maximum production of the pilot bakery, this would mean approximately a two percent increase in the water content of the baking oven vapors. Although the dilution factor is already great, this increase was considered undesirable. Therefore, the gas fired oven was abandoned in favor of an electric oven, sacrificing considerable baking capacity which was then compensated for by extended baking schedules.

A negative pressure system was used to draw the baking oven vapors through the condensation equipment at the rate of two cubic feet per minute based on the exit temperature of the cooled vapors. The oven vapors were passed countercurrently through large water cooled condensers, the condensate being trapped. The cooled vapors were then passed through a salt-ice bath, and finally through a Dewar flask containing dry ice



in carbon tetrachloride.

Eight mixes producing twenty-four pound loaves per mix or 192 pound loaves of bread were baked, collecting 8100 ml of condensate from the baking oven vapors. The specific gravity of the condensate was 1.00 and therefore 8100 gms of condensate were collected. The actual loss of weight of the bread in the oven was 10,886 gms making the efficiency of recovery of the baking oven vapors 74.4 percent, the rest being lost to the atmosphere (opening and closing the oven door, etc.).

#### Separation and Identification of the Mixture

Physical examination of the condensate showed it to be a pale yellow solution, distinctly acid in nature having a pH of 3.5 with a total acidity of 6 ml of 0.1 N sodium hydroxide per 100 ml of solution titrated to an end point using phenolphthalein as the indicator. The low pH of the solution along with the low total acidity suggested the possibility of inorganic acids or acid radicals being present. However, qualitative tests for the chloride, sulfate, and phosphate ions were negative (12). This infers the presence of formic acid to account for the high degree of dissociation present in the absence of inorganic acid radicals.

Organic Class Tests. Group organic class tests were

conducted on the condensate from the baking vapors. The condensate gave a very positive reaction to the ferric hydroxamate test for esters. The phenylhydrazine hydrochloride test for aldehydes and ketones yielded a positive indication. The condensate also produced very positive reactions to Schiff's and Tollen's reagent. Test for alcohols could not be made with the water present. The test for acids could not be conducted because of the presence of esters. However, the presence of acids has already been accounted for. Alcohols are assumed to be present because of the presence of esters under conditions very unfavorable for esterification. Summarizing the findings of the class tests and physical examination of the condensate, it was concluded that the condensate of baking oven vapors contained esters, acids, alcohols, and aldehydes and/or ketones.

Distillation of the Condensate. Direct distillation of the condensate mixture produced a continually rising boiling temperature with much decomposition material resulting. Vacuum distillation produced the same effect, in fact evaporation at room temperature resulted in decomposition. Steam distillation produced no separation of classes. Furthermore it produced very erratic Duclaux numbers, and only resulted in further dilution of the mixture. The inference can be drawn that all the products of the condensate mixture are volatile with steam, (means in which they were collected) and are of the group classification of  $S_1$  (Table 4).



Extraction with Solvents without Chemical Change. Selective solvent extraction experiments were conducted using ether, Skellysolve (hexane), acetone, and carbon tetrachloride. These solvents produced no selective separation of classes, and attempts to concentrate the solvent fraction by distillation or evaporation resulted in decomposition material.

The schematic procedure of separation of organic mixtures containing esters as outlined by Shriner and Fuson (11) was not applicable to the mixture contained in the condensate. On saturation with potassium carbonate it was apparent that the concentration of neutral compounds of group  $S_1$  was not great enough to form a separate layer. It was thought that if a known of group  $S_1$  was introduced (one that was not likely to occur in the mixture) that on separation it would also contain those neutral  $S_1$  components of the mixture. Several such compounds were tried with at least partial recovery of the neutral  $S_1$  fraction. However, all attempts of separation of the resulting fraction resulted in decomposition of the material. It did effect a separation and concentration that might be useful in later procedures.

The point arose as to how concentrated a solution must be before separation could be achieved by this technic. Standard solutions of varying concentration of absolute ethyl alcohol were prepared and the standard solutions were saturated with potassium carbonate. It was found that the threshold concentration at which the ethyl alcohol would separate out into a

separate layer was slightly less than one percent. This would indicate that the concentration of neutral  $S_1$  compounds in the condensate is below one percent.

Extraction by Solvents that Produce Chemical Change. It became apparent, as the work of separation and identification progressed, that a concentration of the minor constituents would have to be achieved before the usual methods of separation and identification could be accomplished. Experiments were conducted, therefore, attempting to form solid derivatives of each class of compounds present in the condensate. Attempts were made to convert the acids to amides with thionyl chloride and ammonia, to form anilides with aniline, and to form the p-nitrobenzyl esters with p-nitrobenzyl bromide. The aldehydes and ketones were subjected to reactions to form semicarbazones, 2-4 dinitrophenylhydrazones, and oximes. However, the extreme dilution of the mixture made reactions impossible to obtain and in the case of alcohols could not even be attempted with water present.

The organic mixture was neutralized with sodium hydroxide and evaporated to dryness. This produced the sodium salts of the acid fraction in the crystalline form. It was noted that a definite color change occurred upon neutralization. Also, no decomposition resulted when the solution was evaporated to dryness. This would indicate that the acids were not thermostable in their original form, or that intermediate products are present in the original mixture. The shifting of the pH results

in the more stable end products. It is also evident that the acid fraction would have to be removed before separation of the other classes could be accomplished.

The sodium salts of the acid fraction were then reacted with ethyl alcohol, successfully forming the ethyl ester of formic and acetic acid. The concentration of other acids was not great enough to enable identification or separation.

Fractional Precipitation of Acids. The process of fractional precipitation of organic acids by the formation of their insoluble lead or magnesium salts must be conducted in saturated alcoholic solutions. The extreme amounts of water in the organic mixture made fractional precipitation of the acid fraction impossible.

Chromatographic Technics. Chromatographic experiments were conducted using the three methods described for the preparation of the unknown solutions to be separated. For each method of preparation of the unknowns, chromatograms were developed using both ascending and descending technics. The concentration of each unknown was varied, for each solvent applicable for the unknown being separated, by spotting the paper with 1 to 15 applications of the 0.01 ml pipet. The length of time of development was varied from 3 to 24 hours for each concentration of unknown applied to the paper for development. Known acids were developed with each unknown determination.

The use of paper chromatographic technics did not achieve the desired separation and identification. The acid spots would (a) not move at all along the paper, (b) move all the way with the solvent front, or (c) be streaked along the paper from top to bottom. It is believed by the author that the unequal concentration of the acids was the factor preventing their separation.

#### SUMMARY

The vapors produced by bread during baking in the oven have been studied, after collection by three different methods. In addition numerous means of separation and identification of the components of the baking oven vapors were investigated. From these studies the following information has been obtained:

1. The most effective means of collecting a sample of baking oven vapors is by the condensation method. Collection by liquid absorption and solid adsorption on activated charcoal produced a less concentrated sample of the baking oven vapors than did the condensation method.

2. It was shown that the baking oven vapors consist of water, alcohols, acids, esters, and aldehydes and/or ketones.

3. The acids present in the condensate from the baking oven vapors produced a solution whose pH was 3.5 and total acidity was 6 ml of 0.1 N NaOH per 100 ml of condensate

solution. Of the acids present in the condensate, formic and acetic acid were separated and identified. The absence of inorganic acids was established.

4. It was shown that the concentration of products and byproducts of alcoholic fermentation contained in the baking oven vapors condensate was less than one percent.

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## APPENDIX

### Suggestions for Future Study

From the investigation of the baking oven vapors it is seen that combinations of the different methods of separation and identification will have to be employed.

The most useful starting point for the identification of the acid fraction of the condensate obtained in the experiments conducted would be the formation of the sodium salts of the acids. Recourse could be had to the fractional precipitation of the acids by use of lead or magnesium acetate, using saturated alcoholic solutions of the sodium salts of the acids. If the minor acids present cannot be separated by this method, it seems certain that formic and acetic acid could be separated from the other acids present. With the removal of formic and acetic acid, the chromatographic technics for volatile fatty acids could be employed on the remaining fraction.

The concentration of the neutral components by means of seeding with a known substance could be used as the starting point for the separation and identification of this fraction. Either derivatives could be formed or chromatographic technics could be employed.

Selective oxidation of the aldehydes, ketones and alcohols to acids might be accomplished, and the technics developed for the separation of the acids could be employed.

A STUDY OF BAKING OVEN VAPORS

by

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B. S., Kansas State College  
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Investigations of methods for collecting the vapors produced by bread in the oven showed that condensation of the vapors produced a higher concentration of fermentation products and by-products than did liquid absorption or solid adsorption.

The investigations on separation and identification of the components of the condensate collected were only partially successful. It was shown, however, that the condensate contained esters, acids, alcohols, and aldehydes and/or ketones. It was also shown that the baking oven vapors appearing in the condensate contained less than one percent of these products.

The components of the condensate were found to be very unstable to heat, and that on an increase in the pH of the condensate a more stable form of these components was produced.

The acids present in the original condensate produced a pH of 3.5 and a total acidity of 6 ml of 0.1 N sodium hydroxide per 100 ml of condensate titrated to an end point using phenolphthalein as an indicator. The absence of inorganic acids were established, and formic and acetic acid were separated and identified.